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Abstract

We present a method to describe the relationship between dry particle diameter and cloud condensation nuclei (CCN) activity using a single hygroscopicity parameter. Values of the hygroscopicity parameter are between 0.5 and 2 for highly-CCN-active salts such as sodium chloride, between 0.01 and 0.5 for slightly to very hygroscopic organic species, and 0 for nonhygroscopic components. If compositional data are available and if the hygroscopicity parameter of each component is known, a multicomponent hygroscopicity parameter can be computed by weighting component hygroscopicity parameters by their volume fractions in the mixture. In the absence of information on chemical composition, experimental data for complex, multicomponent particles can be fitted to obtain the hygroscopicity parameter. The hygroscopicity parameter can thus also be used to conveniently model the CCN activity of atmospheric particles, including those containing insoluble components. We confirm the general applicability of the hygroscopicity parameter and its mixing rule by applying it to published hygroscopic diameter growth factor and CCN-activation data for single- and multi-component particles.

1 Introduction

Simple and accurate descriptions of cloud condensation nucleus (CCN) activity of complex atmospheric aerosols are needed to better constrain cloud resolving models, chemical transport models and global climate simulations (e.g., Koch, 2001; Chung and Seinfeld, 2002; Bilde and Svenningsson, 2004; Liu et al., 2005). Köhler theory (Köhler, 1936) predicts CCN activity based on the aerosol physicochemical properties, i.e. solute mass, molecular weight, bulk density, dissociable ions, and activity coefficient. Inorganic compounds, which are generally effectively modeled by the parameters and assumptions used in Köhler theory, are ubiquitous in atmospheric particulate matter, but it was recognized some time ago that less- and nonhygroscopic

ACPD

6, 8435–8456, 2006

organic compounds can contribute substantially to, and sometimes even dominate, atmospheric aerosol mass concentrations. Particularly for aerosols that are not sampled close to emissions, it has been found that most particles do not consist of a single component, but rather that organic and inorganic constituents are usually found in the same particles (Murphy et al., 1998).

Early descriptions of internally-mixed particles conceptually decomposed the particle into an insoluble and nonhygroscopic core immersed in an aqueous-ionic solution of some assumed composition, usually sodium chloride or ammonium sulfate (Junge and McLaren, 1971; Fitzgerald, 1973). Although this description sometimes improves comparisons between measured and modeled CCN activity, it cannot explicitly treat the variations in hygroscopic growth attributable to water soluble organic carbon, including constituents originating from biomass burning and secondary organic aerosol formation. This gap was filled by extensions of Köhler theory (Shulman et al., 1996; Kulmala et al., 1997; Laaksonen et al., 1998). However, application of the extended theories requires that the properties of all participating compounds are known. Although this approach has been applied successfully to laboratory data for single-component and some multicomponent particles (Raymond and Pandis, 2002, 2003; Bilde and Svenningsson, 2004; Huff Hartz et al., 2006; Svenningsson et al., 2006), insufficient data are available to initialize calculations for ambient aerosols containing a multitude of generally unspeciated organic compounds. Further, results of experiments studying the hygroscopicity or CCN activity of lab-generated or atmospheric particles are often presented in terms of either the critical diameter for activation at a specified water vapor supersaturation (relative humidity, RH, >100%), or the diameter hygroscopic growth factor (RH<100%). Although variations in these parameters qualitatively express the relative hygroscopicity of the tested particles, critical diameters and growth factors themselves are not readily applied quantitatively in modeling studies.

Here we propose the use of a hygroscopicity parameter, κ, that represents a quantitative measure of aerosol water uptake characteristics and CCN activity. Values for κ for specific compounds, or for arbitrary mixtures, can be determined experimentally by

ACPD
6, 8435–8456, 2006

fitting CCN activity or hygroscopic growth factor data. The definition is consistent with traditional Köhler theory but the concept does not rely on a priori assumptions about the density, molecular weight and activity coefficients of the individual compounds.

2 κ–Köhler theory

The saturation ratio, S, over an aqueous solution droplet can be calculated from

$$S = a_w \exp\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D}\right), \quad (1)$$

where a_w is the activity of water in solution, ρ_w is the density of water, M_w is the molecular weight of water, $\sigma_{s/a}$ is the surface tension of the solution/air interface, R is the universal gas constant, T is temperature, and D is the diameter of the droplet. The hygroscopicity parameter is defined through its effect on the water activity of the solution:

$$\frac{1}{a_w} = 1 + \kappa\frac{V_s}{V_w}, \quad (2)$$

where V_s is the volume of the dry particulate matter and V_w is the volume of the water. For a multicomponent system (multiple solutes + water) at equilibrium, for which the Zdanovskii, Stokes, and Robinson (ZSR) assumption applies, the total volume of the water is the sum of the water contents due to the individual components, i.e. $V_w = \sum V_{wi}$, and the individual V_{wi} are obtained for $a_{wi} = a_w$. Applying the ZSR assumption and rearranging Eq. (2) for V_w gives:

$$V_w = \frac{a_w}{1 - a_w}\sum_i \kappa_i V_{si}, \quad (3)$$

ACPD
6, 8435–8456, 2006

The total volume of the system (water + solute) is

$$V_T = \sum_i V_{si} + \sum_i V_{wi} = V_s + V_w \tag{4}$$

Defining the individual (dry) component volume fractions as $\varepsilon_i = V_{si}/V_s$ and recognizing that $V_w = V_T - V_s$ Eq. (3) becomes

$$V_T - V_s = \frac{a_w}{1 - a_w} V_s \sum_i \varepsilon_i \kappa_i \tag{5}$$

The solute (dry) and total volumes can be converted to their sphere equivalent diameters, $D_d^3 = 6V_s/\pi$ and $D^3 = 6V_T/\pi$, respectively. Solving Eq. (5) for a_w and combining the result with Eq. (1) yields the equation defining "κ-Köhler theory":

$$S(D) = \frac{D^3 - D_d^3}{D^3 - D_d^3(1-\kappa)} \exp\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D}\right), \tag{6}$$

where the overall value for κ is given by the simple mixing rule

$$\kappa = \sum_i \varepsilon_i \kappa_i. \tag{7}$$

The critical supersaturation (s_c, where $s_c = S - 1$ and is usually expressed as a percentage) for a selected dry diameter of a particle having hygroscopicity κ is computed from the maximum of the κ-Köhler curve (Eq. 6). Figure 1 shows the relationship between dry diameter and critical supersaturation for a range of constant κ values. The curves follow the expected Köhler slope of $-3/2$ when $\log(D_d)$ is plotted on the abscissa and $\log(s_c)$ on the ordinate, for $\kappa > 0.01$. As will be shown in the next section, $\kappa \sim 2$ is an upper limit for the most hygroscopic species typically found in the atmospheric aerosol (e.g., sodium chloride). Lower values of κ then indicate less-hygroscopic, or less CCN-active, behavior, with approximately three orders of magnitude spanning the $s_c - D_d$

ACPD
6, 8435–8456, 2006

space relevant to the atmosphere. As κ approaches zero, the particle becomes nonhygroscopic and the slope approaches that expected for an insoluble but wettable particle, i.e. −1. This can also be seen mathematically from Eq. (6): for κ=0, the water activity a_w=1, representing wetting of the dry particle by a pure water film, and Eq. (6) reduces to the so-called Kelvin equation.

3 Derivation of κ values for atmospherically-relevant species and particle types

In Fig. 2 we show experimentally-determined critical supersaturations as a function of dry particle diameter for several single- and multi-component particle types, as reported by Svenningsson et al. (2006) and Dinar et al. (2006). The data follow, to a good approximation, the slopes of the constant-κ lines, and have relative κ values as expected: κ values for hygroscopic inorganic species (ammonium nitrate) and mixtures containing appreciable amounts of inorganics are close to the κ=1 line, whereas moderately hygroscopic organic species have CCN activities corresponding to $0.01<\kappa<0.5$ The dashed lines indicate best-fit values of κ, which can be determined by fitting observed values of s_c to the maxima of Eq. (6) for the corresponding dry diameter. If $\kappa>0.01$, then κ alternatively can be calculated from paired s_c–D_d values from the following approximate expression:

$$\kappa = \frac{4A^3}{27D_d^3 \ln^2 s_c}$$
$$A = \frac{4\sigma_{s/a}M_w}{RT\rho_w} \quad (8)$$

Table 1 lists the values of κ determined from the data in Fig. 2, along with best-fit values for ammonium sulfate and sodium chloride. For these salts, we do not fit κ to experimental values, as these compounds are commonly used for the calibration of CCN instruments and thus the "experimental" values simply reflect the choice of water activity expression used in the calibration. Instead, a best-fit κ is determined from s_c – D_d relationships computed from Eq. (1), where a_w as a function of composition for the

ACPD
6, 8435–8456, 2006

aqueous solutions is obtained from the Aerosol Inorganic Model (Clegg et al., 1998). Table 1 also shows the range of κ reported for typical experimental uncertainties, for the calibration salts as well as for the other particle types where available.

For a multicomponent particle of known composition, Eq. (7) suggests that the κ value expressing its CCN activity can be estimated from the κ values for each constituent. Some limited data on the CCN activity of mixed particles that can be used to test the validity of this mixing rule are available in the literature (Raymond and Pandis, 2003; Broekhuizen et al., 2004; Svenningsson et al., 2006). In Table 1 we list derived κ values for individual components, and compare predicted and measured κ values in Fig. 3. Mass fractions were converted to volume fractions using bulk density values. Uncertainties in individual component κ values were propagated to the prediction in quadrature. An example calculation for a mixed particle is shown in Table 2. In general, the predictions from Eq. (7) are within experimental uncertainties, confirming the applicability of the underlying assumptions.

For a multicomponent particle with at least one component having κ=0, the critical supersaturations predicted from Eqs. (6) and (7) should be identical to those predicted by a version of Köhler theory that treats insoluble cores immersed in an aqueous ionic solution (e.g., Snider et al., 2003). In Fig. 4 we demonstrate that the supersaturations calculated from Eqs. (6) and (7) for a 0.1 μm particle are identical to those predicted by the Snider et al. (2003) formulation.

It must be pointed out that the determination of a value for κ from observational data using either Eq. (6) or (8) requires the assumption of a solution surface tension. In all cases shown here, we have assumed $\sigma_{s/a}$=0.072 J m^{-2}. It is now well known that some constituents of the atmospheric aerosol are surface active and can suppress surface tension, sometimes to a significant extent (Facchini et al., 1999; Svenningsson et al., 2006). Use of a lower value of surface tension would result in a decrease in the derived value of κ, but since the lower surface tension must also be applied to any subsequent determination of s_c, predictions of CCN activity for surface-active components are not affected. For example, Fig. 2 suggests that the CCN activity of fulvic acid, which is

ACPD
6, 8435–8456, 2006

known to strongly reduce surface tension in bulk samples (Svenningsson et al., 2006) is modeled effectively assuming $\sigma_{s/a}$=0.072 J m^{-2} in the estimation of κ.

It is not straightforward to apply bulk sample-based parameterizations to curved droplets, where partitioning between the bulk and the surface leads to complicated thermodynamics (Sorjamaa et al., 2004). Furthermore, if surface-active components are present in mixed particles even bulk surface tensions are not readily predictable (Topping et al., 2005). In our approach, the derived value of κ for fulvic acid is biased large since we assumed $\sigma_{s/a}$=0.072 J m^{-2}. However, the larger κ value for this component partially compensates for the lowered surface tension of the mixture. Although this approach is not thermodynamically rigorous, it appears to work well for mixtures that contain surface active and surface inactive compounds, as is shown in Fig. 3. For this reason, we believe the use of $\sigma_{s/a}$=0.072 J m^{-2} to fit all data represents a reasonably-accurate description of hygroscopic behavior of both single components and mixtures, but further testing of this assumption is needed.

4 Links between hygroscopic growth factor and critical supersaturation

Equation (6) can be used to approximate the size of a particle, characterized by a constant value of κ, in equilibrium with a specified water vapor saturation for both sub- and super-saturated conditions. In general, however, experimental data for water activities over the full range of solution concentrations cannot be well-fit with Eq. (2) using a constant κ. For example, Kreidenweis et al. (2005) used a polynomial to model variations in κ for a_w<0.95, and then extrapolated that polynomial to dilute conditions (a_w approaching 1) to estimate the critical supersaturation. In that study, water activity data for RH<100% were obtained using a humidified tandem differential mobility analyzer (HTDMA, Brechtel and Kreidenweis, 2000). Extrapolated $s'_c s$ using this or similar methods (e.g., Svenningsson et al., 2006) are in good agreement with measured $s'_c s$ for many, but not all, particle types studied thus far (Kreidenweis et al., 2005; Koehler et al., 2006; Petters et al., 2006; Svenningsson et al., 2006). It has been recognized some

ACPD
6, 8435–8456, 2006

time ago, however, that hygroscopicity is subordinate to particle size with respect to cloud droplet activation properties (Fitzgerald, 1973). Small, and in some cases, moderate variations in κ have little to no effect on the fraction of activated droplets, when the activation of a population of particles in a parcel experiencing changing supersaturations is simulated (Ervens et al., 2005; Koehler et al., 2006). Thus, we hypothesize that a constant κ is likely sufficient to adequately treat aerosol-water interactions in both the sub- and supersaturated domains. If this is true, then κ may be derived either by fitting CCN activity data, as described above, or from HTDMA-determined values of the hygroscopic diameter growth factor, *gf*, as a function of relative humidity, *RH*, that have been fit to a rearranged version of Eq. (6):

$$\frac{RH}{\exp\left(\frac{A}{D_d gf}\right)} = \frac{gf^3 - 1}{gf^3 - (1-\kappa)} \tag{9}$$

where *RH* has been expressed as a fraction.

In Fig. 5 we compare κ values derived from HTDMA data with those derived from CCN activity measurement, for a variety of particle compositions for which both types of data appeared in the literature (see Table 1 for sources). The agreement is within 30% for most compounds, indicating that the change in κ from a_w~0.9 to a_w at CCN activation is small. Furthermore, this difference in κ, although undoubtedly present, appears to not be effectively resolved using current measurement techniques, as can be seen by the sometimes substantial uncertainties in the inferred κ.

For some of the compounds shown in Table 1, e.g. adipic or succinic acid, no growth factors were measured. The current detection limit for this measurement is ~1.02, placing a lower limit of κ~0.006 that can be observed in the subsaturated domain. A quick comparison between growth factor derived and CCN derived κ values for these compounds shows, however, that κ<0.006 does not match the much larger values inferred from their CCN activity. While the hygroscopicity of succinic and adipic acid is fairly large (κ>0.1), their solubility in water, i.e. the mass of solute that can be dissolved in a given amount of water, is small. The equilibrium water content of a succinic acid

ACPD
6, 8435–8456, 2006

particle at a_w~0.9 corresponds to a metastable state where the concentration of solute exceeds the solubility limit. An initially dry particle will not be deliquesced at the corresponding *RH* and thus no water uptake can be observed. In the case of adipic acid the solubility limit is so low that the water activity of the saturated solution exceeds a_w>0.97. Then CCN activation will be controlled by the solubility limit instead of its intrinsic hygroscopicity and data for these compounds do not observe the −3/2 rule shown in Fig. 1 (Kreidenweis et al., 2006). Laboratory studies have shown that it is quite difficult to obtain pure, dry compounds for which activation is controlled by the solubility limit, since trace amounts of water or soluble compounds readily lead to metastable solution droplets and hygroscopicity controlled activation (Hori et al., 2003; Bilde and Svenningsson, 2004; Broekhuizen et al., 2004; Huff Hartz et al., 2006). Although the phase state of aerosols in the atmosphere is not precisely known, it seems reasonable to assume that metastable states dominate, especially because most particles exist as internal mixtures in the atmosphere (Murphy et al., 1998).

5 Summary and conclusions

We propose the use of a hygroscopicity parameter, κ, for purposes of characterizing the relative hygroscopicities of individual aerosol constituents, known mixtures, and complex atmospheric aerosols. The hygroscopicity parameter is used to model the composition-dependence of the solution water activity, and when combined with the Kelvin term into "κ-Köhler theory", determines the equilibrium water vapor saturation ratio, S, over an aqueous droplet. As with traditional Köhler theory, the maximum in $S(D)$ computed for a specified initial dry particle size and composition (expressed by κ) determines the particle's critical supersaturation (s_c) for activation to a cloud droplet.

Fits to theoretical s_c–D_d relationships are used to show that 0.5<κ<2 for hygroscopic inorganic species, such as ammonium sulfate and sodium chloride. In contrast, experimental s_c–D_d data for organic species and their mixtures span a wider range of hygroscopicities and are best fit to lower values of κ, 0.01<κ<0.5. We use pub-

ACPD
6, 8435–8456, 2006

lished data to show that the κ values describing the hygroscopic behavior of multi-component particles can be derived by volume-weighting the best-fit κ values for the individual constituents. This mixing rule holds even when one or more components are nonhygroscopic (κ=0), namely, the equations presented here predict the same critical supersaturations as do extensions of Köhler theory that treat insoluble cores.

In contrast to traditional formulations of Köhler theory, use of the hygroscopicity parameter to compute s_c obviates the need to determine, or assume, aerosol properties such as dry particle density, molecular weight, and dissociation constants. That is, data for the s_c–D_d relationships observed for model or actual atmospheric aerosols can be conveniently fit by a single parameter. We suggest that κ may be useful in streamlining aerosol compositional models, including those that link to drop activation schemes, as well as enable such models to handle the hygroscopic properties of complex aerosol types that were heretofore difficult to fit to traditional Köhler parameters. We suggest that κ may be fit to CCN data assuming $\sigma_{s/a}$=0.072 J m^{-2}. This approach appears adequate for predicting CCN activity of mixed particles having appreciable amounts of strongly surface active materials, but the generality of this assumption requires further verification.

Although the focus of this paper is on characterizing the CCN activity of atmospheric particulate matter, it is possible to also derive values of κ from other types of data, such as hygroscopic growth factor data obtained from an HTDMA. We show that values of κ derived from published HTDMA data are consistent with those derived by fitting published CCN activity data. The level of agreement for the limited available data is generally within experimental errors and probably within the range of $\delta\kappa$ for which minimal effects on activated drop fractions are observed. However, the resolution in κ that is required to address outstanding problems in aerosol indirect effects on climate is not yet well-established, and further research on quantifying acceptable uncertainities in κ is needed.

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Table 1. Growth factor derived and CCN derived κ. Values in the subsaturated domain were derived from growth factors at the highest measured water activity, typically a_w~0.9. Values in the supersaturated domain were derived from CCN measurements between 0.3%<s_c<1%. Uncertainty calculation varied from study to study and is described in the footnotes. N/A denotes not available.

Compound	Growth factor derived κ			CCN derived κ		
	κ_{low}	κ_{mean}	κ_{up}	κ_{low}	κ_{mean}	κ_{up}
$(NH_4)_2SO_4$	0.33[6]	0.53	0.72[6]	N/A	0.615[13]	N/A
NH_4NO_3	N/A	N/A	N/A	0.577	0.665[10]	0.753
NaCl	0.91[6]	1.12	1.33[6]	N/A	1.274[13]	N/A
malonic acid	0.28	0.44[6]	0.6	0.199	0.227[11]	0.255
glutaric acid	0.12	0.2[6]	0.28	0.054 0.113	0.088[5] 0.195[8]	0.016 0.376
glutamic acid	N/A	0.154[5]	N/A	0.013 0.016	0.183[5] 0.248[8]	0.319[5] 0.418[8]
succinic acid	N/A	<0.006[12]	N/A	0.166	0.231[4]	0.295
adipic acid	N/A	<0.006[14]	N/A	N/A	0.096[1]	N/A
levoglucosan	0.15	0.165[6]	0.18	0.193	0.208[10]	0.223[10]
phthalic acid	N/A	0.059[5]	N/A	0.022	0.051[5]	0.147
homophthalic acid	N/A	0.081[5]	N/A	0.048	0.094[5]	0.212
leucine	N/A	N/A	N/A	0.001	0.002[8]	0.003
pinic acid	N/A	N/A	N/A	0.162	0.252[8]	0.422
pinonic acid	N/A	<0.006[12]	N/A	0.067	0.111[8]	0.201
norpinic acid	N/A	N/A	N/A	0.118	0.187[8]	0.323
poly(acrylic acid)	N/A	0.060[2]	N/A	0.040	0.051[7]	0.068
Suwanee River fulvic acid	N/A	0.056[2] 0.044[12]	N/A	0.057 0.050 0.029	0.067[10] 0.056[3a] 0.033[3b]	0.077 0.063 0.037

ACPD
6, 8435–8456, 2006

Table 1. Continued.

[1] Broekhuizen et al. (2004), uncertainty not available, κ was calculated for the pure metastable adipic acid data point
[2] Brooks et al. (2004), uncertainty not available
[3] Dinar et al. (2006), uncertainty evaluated from $\pm D_c$; a: untreated; b fractionated 10–30 kDa
[4] Hori et al. (2003), uncertainty evaluated from spread in data
[5] Huff Hartz et al. (2006), uncertainty evaluated from $\pm D_c$, mass growth factor were converted to size growth factors
[6] Koehler et al. (2006), range of κ from Table 3
[7] Petters et al. (2006), uncertainty evaluated from $\pm s_c$
[8] Raymond and Pandis (2002), uncertainty evaluated from $\pm D_c$
[9] Raymond and Pandis (2003), uncertainty evaluated from $\pm D_c$
[10] Svenningsson et al. (2006), uncertainty evaluated from spread in data
[11] Kumar et al. (2003), uncertainty evaluated from spread in data
[12] Chan and Chan (2003), κ estimated from mass growth factors, *gf*'s for succinic and pinonic acid were below the detection limit
[13] Clegg and Wexler (1998), critical supersaturation calculated from the aerosol inorganic model
[14] Prenni et al. (2003), *gf*'s for adipic acid were below the detection limit

ACPD
6, 8435–8456, 2006

Table 2. Example mixture calculation for the mixture "MIXORG" in Svenningsson et al. (2006). Measured hygroscopicity was κ=0.125±0.016. Uncertainty in the prediction was calculated in quadrature. N/A denotes not available.

Compound	$\kappa \pm \sigma_\kappa$	weight fraction	density (kg m^{-3})	volume fraction
levoglucosan	0.208±0.015	0.2	1600	0.207
succinic acid	0.231±0.064	0.4	1570	0.405
fulvic acid	0.067±0.010	0.4	1500	0.388
$\kappa = \sum \kappa_i \varepsilon_v$	0.163±0.042	1	N/A	1

ACPD
6, 8435–8456, 2006

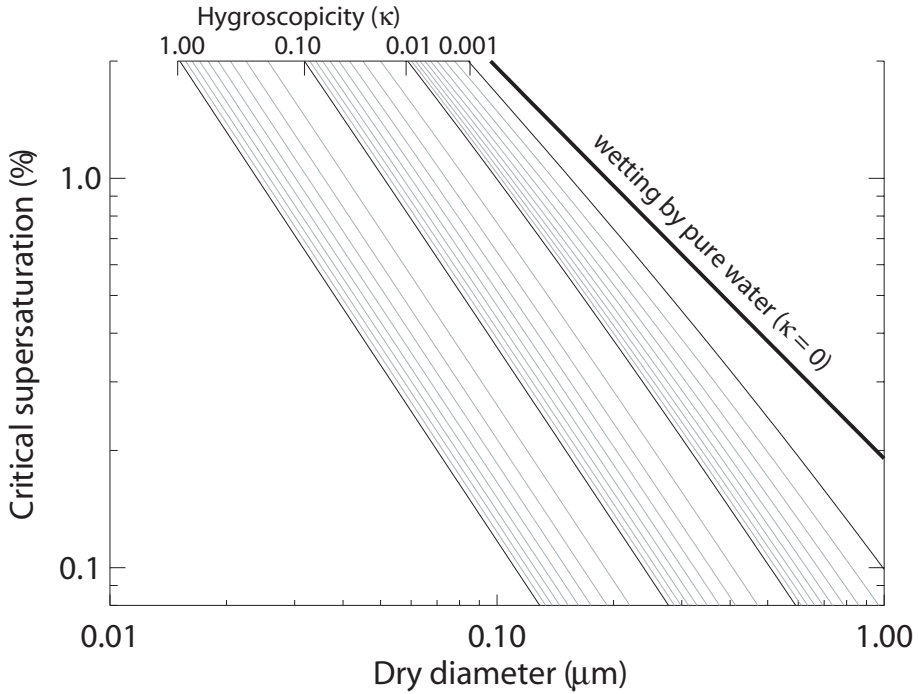

Fig. 1. Calculated critical supersaturation for $0<\kappa<1$. The gray lines are linearly spaced intermediates.

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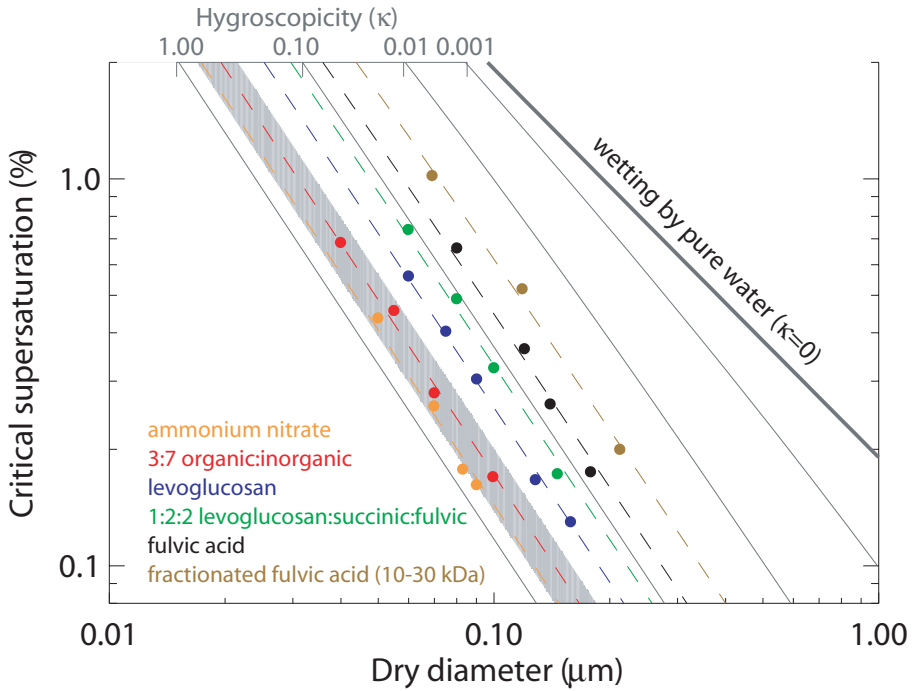

Fig. 2. s_c–D_d data for pure compounds, organic mixtures and organic-inorganic mixtures. Data are taken from Svenningsson et al. (2006) and Dinar et al. (2006). The 3:7 organic:inorganic mixture is the "polluted" mixture from Svenningsson et al. (2006). Dashed lines indicate best-fit κ values for each particle type. Shaded area indicates reported range of values for ammonium sulfate (Table 1).

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6, 8435–8456, 2006

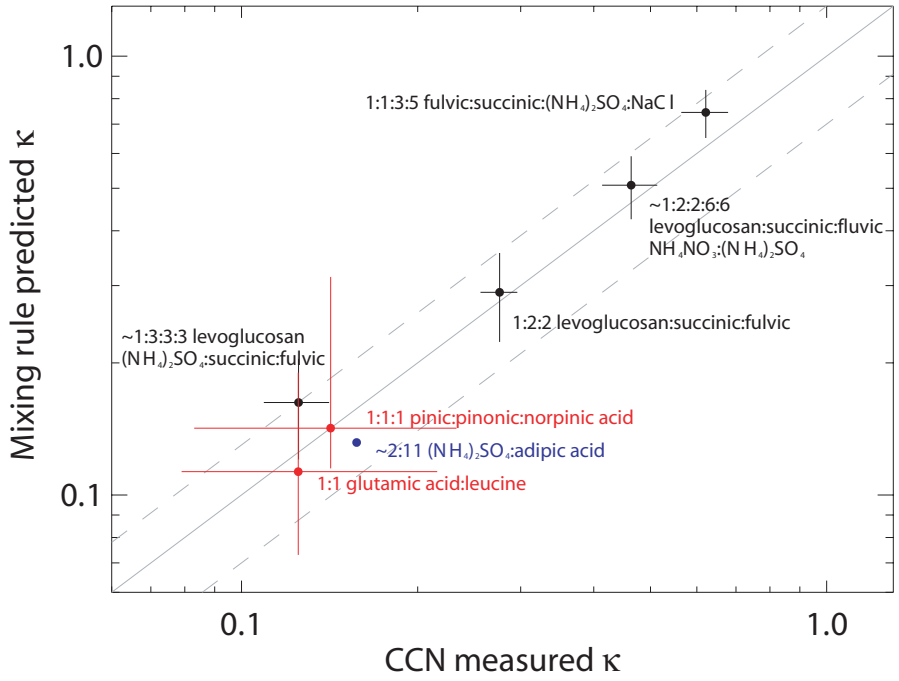

Fig. 3. Values of κ for multicomponent particles, predicted from the linear mixing rule (ordinate) and estimated from CCN activity measurements (abscissa). Measurement-derived κ values were fit using $\sigma_{s/a}$=0.072 J m^{-2}. Black points: Svenningson et al. (2006); red points: Raymond and Pandis (2003); blue point: Broekhuizen et al. (2004). Indicated component ratios are mass ratios. The value and origin of each individual-component κ applied in the mixing rule is given in Table 1. Vertical and horizontal bars show an estimate of the uncertainty in measured and predicted κ. Dashed lines indicate ±30% deviation from the 1:1 line.

ACPD
6, 8435–8456, 2006

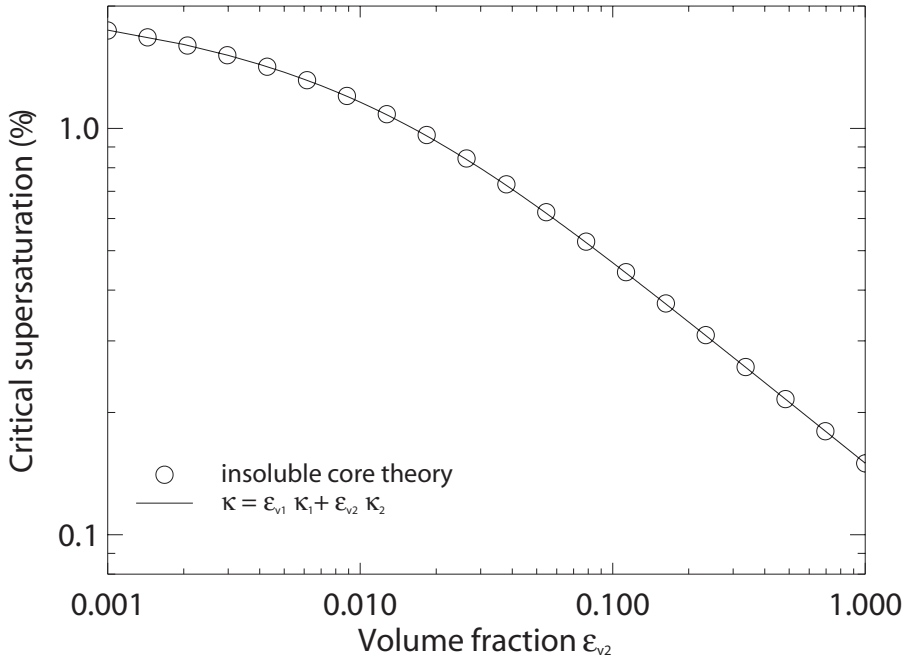

Fig. 4. Calculated critical supersaturations for different values of ε_{v2} using insoluble core theory (Snider et al., 2003, open symbols) and κ-Köhler theory (Eqs. 7 and 8, solid lines). Assumed values are D_d=0.1 μm, κ_1=0, κ_2=0.615.

ACPD
6, 8435–8456, 2006

One parameter representation for aerosol-water interactions

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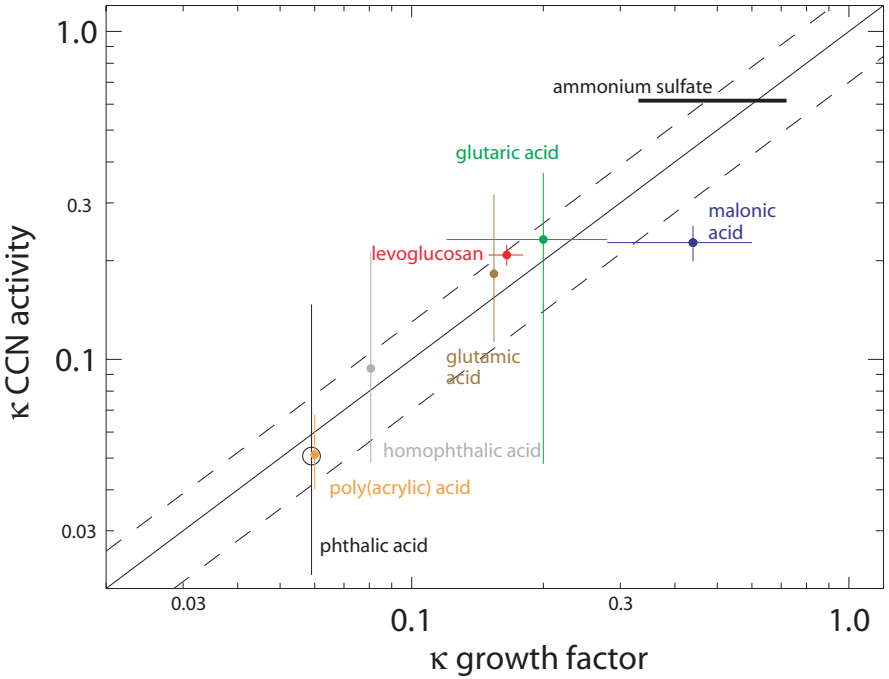

Fig. 5. Values of κ for indicated particle types, estimated from *gf* data and Eq. (8) (abscissa) and estimated from CCN activity measurements (ordinate). All κ values were fit using $\sigma_{s/a}$=0.072 J m^{-2}. Data sources are summarized in Table 1. Vertical and horizontal bars show an estimate of the uncertainty in κ. Dashed lines indicate ±30% deviation from the 1:1 line.

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